Synopsis of the Ph.D. Thesis
Titled

Study of Structural, Electrical, Magnetic and Mössbauer Properties of Aluminium and Indium Substituted Mg-Mn-Ni Ferrite Synthesized via Citrate Precursor Technique

Submitted by
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❖ Introduction

Applications of nanoferrites are growing in leaps and bounds with the advancement in nanotechnology [1]. Spinel ferrites have been extensively investigated in recent years for their useful electrical, dielectric and magnetic properties. Magnetic properties of spinel ferrite depend on distribution of cations among two sub-lattices, tetrahedral A-site and octahedral B- site [2, 3]. In Mg-Mn ferrite, if Fe^{3+} ions are replaced by In^{3+} ions and Al^{3+} ions, magnetic properties are modified [4-7]. Synthesis of nanometer-sized particles proved to be one of the interesting fields of material science in material processing and technological applications, as small size particles have some of the interesting properties as compared to bulk particles [8]. Ferrites are extensively used in microwave applications because of their high resistivity and low eddy current losses [9]. Metallic ions can occupy two types of sites: tetrahedral A-site, where each metallic ion is surrounded by four oxygen ions and octahedral B-site, where each metallic ion is surrounded by six oxygen ions [10].

The resistivity of a ferrite is an important property, since it determines its performance at high frequencies, where eddy current losses may be high, resulting in a significant loss of energy. High value of dc resistivity ($10^8\Omega$-cm) makes this ferrite more effective in high frequency applications. It is very important in many applications to control the dc resistivity of the spinel ferrites. For this purpose three major possibilities are available, controlling the sintering temperature, selection of basic ferrite and substitution by appropriate dopant. The dielectric constant of any materials, in general, is directly related to dielectric polarization. Higher the polarization, higher is the dielectric constant of the material. There are four primary mechanisms causing polarizations: electronic polarization, ionic polarization, dipolar polarization and space charge polarization. Their occurrence depends upon the frequency of the applied field. The

important magnetic properties of spinel ferrites mainly depend on the magnetic interactions between cations with magnetic moments that are situated in the tetrahedral A-site and the octahedral B-site. The magnetic order in the cubic spinel ferrite is due to super exchange interaction mechanism occurring between the metals ions in the tetrahedral A and octahedral B sub-lattices. The A-A interaction as well as the B-B interaction exist but they are very weak. Since the A-B interactions are the strongest, it will align all the magnetic moments at the A-site in one direction and those at B-site in the opposite direction, thus constituting two saturated and oppositely magnetized sub-lattices at 0K. The resultant magnetization is, therefore, the difference between the magnetization of B and A sub-lattices, the former generally having larger value.

Many workers have investigated In^{3+} and Al^{3+} substituted Mg-Mn [12] ferrites but a relatively small literature is available on the indium and aluminium substituted Mg-Mn-Ni ferrite.

Mg-Mn-Ni ferrite may emerge as one of the most important material due to its high dc resistivity, very low relative loss factor of the order of 10^{-6}-10^{-5} and low dielectric losses. In^{3+} and Al^{3+} doped Mg-Mn-Ni ferrites are prepared by citrate precursor technique without compromising with the desired properties like resistivity, dielectric loss, initial permeability, saturation magnetisation, residual magnetisation and relative loss factor.

❖ Aim of the present work

(1) To prepare the series of In^{3+} and Al^{3+}doped Mg-Mn-Ni ferrite by citrate precursor technique of the compositions

(a) $Mg_{0.2}Mn_{0.5}Ni_{0.3}In_xFe_{2-x}O_4$ (x=0.0, 0.10, 0.15, 0.20, 0.25 and 0.30)

(b) $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ (y=0.0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30)

(2) To characterize all the samples for their structural, electrical, dielectric, magnetic and Mössbauer properties.

(3) To understand and interpret the results on the basis of various possible mechanisms and

models.

❖ **Experimental Details**

- Chemicals were weighed in stoichiometric proportions. Solution of iron (III) citrate was prepared in distilled water by heating at 40^{o}C under continuous stirring. Solutions of magnesium nitrate, manganese nitrate, nickel nitrate and indium nitrate were also prepared separately in distilled water by heating at 40^{o}C under continuous stirring. Citric acid was added to these solutions. These solutions were heated at 40^{o}C for 30 minute and then added to iron citrate solution. Precursor mixture was evaporated to dryness at 40^{o}C to obtain transparent brown colour glossy materials, containing constituent metal ions homogeneously mixed at atomic level. Dried citrate precursor was pre-sintered for 2h at 500^{o}C at rate of 250^{o}C/h to obtain the ferrite powder.
- Pre-sintered powders were mixed with organic binder poly-venyl alcohol (2% by weight) and pressed into pellets by applying a pressure of 5 ton to get pellets having 1.0 cm diameter and 0.15 cm thickness. Toroids/ring of these ferrites having thickness of 2mm and ratio of outer diameter to inner diameter equals 1.5 were formed under pressure of 5 tons.
- Prepared samples were sintered in air at 1200^{o}C at the heating rate of 250^{o}C/h for 1-2 hour in a box type furnace and were subsequently cooled to room temperature. Pellets were coated with silver paste to make electric contact for electrical measurements. Initial permeability and dielectric properties were measured using an Agilent Technologies 4285A Precision LCR Meter.
- Dc resistivity was measured using KEITLEY 2611 System Source Meter. X-ray diffraction studies were made by Cu-K_{α} radiation of wavelength λ=1.54060 Å using

XPERT PRO-system. High resolution transmission electron micrograph was obtained with a JEOL electron microscope.

- M–H studies were carried out by VSM. ^{57}Fe Mössbauer measurements were carried out in transmission mode with ^{57}Co/Rh radioactive source in constant acceleration mode using standard PC-based Mössbauer spectrometer equipped with Weissel velocity drive. Velocity calibration was done with natural iron absorber. The spectra were analyzed using least square fitting programme NORMOS (SITE/DIST).

❖ Physical and structural properties

➢ In^{3+} and Al^{3+} doped Mg-Mn-Ni ferrite

- **Bulk Density**: Bulk density (d_{bulk}) of the samples has been measured using Archimedes principle.
- **XRD Density**: XRD density ($d_{x\text{-}ray}$) of the samples has been calculated by using lattice parameters.
- **Porosity**: Porosity of the samples has been calculated from bulk density (d_{bulk}) and XRD density ($d_{x\text{-}ray}$).
- **X-rays diffraction**: Structural and lattice parameters of samples have been studied using X-rays diffraction.
- **Transmission electron micrograph**: Grain size and surface morphology of samples has been studied using TEM.

❖ Magnetic, electric and dielectric properties

➢ In^{3+} and Al^{3+} doped Mg-Mn-Ni ferrite

- Saturation magnetization of the samples has been measured at room temperature.

- Cation distribution analysis: The cation distribution in the present system is derived from the site preference energy and magnetization method.
- Mössbauer Spectroscopy of samples: To find isomer shift, line width, hyperfine interaction, quadrupole splitting of all the samples.
- Initial Permeability and relative loss factor has been studied as a function of frequency (75 kHz-30MHz) at room temperature.
- Dc resistivity of samples has been studied at different temperatures using two probe method.
- Dielectric constant and dielectric loss of the samples has been studied as a function of frequency (75 kHz-30MHz) and temperature.

❖ Measurements and instrumental details.

- **Synthesis of Samples**
- Both the series of samples have been prepared at Department of Physics, Himachal Pradesh University, Shimla.
- **Physical, structural and micro structural measurements**
- X-rays diffraction of different samples has been done by using XPERT PRO-system at SAIF-CIL Punjab University Chandigarh.
- The grain size and morphology of the samples has been investigated by TEM at SAIF-CIL Punjab University Chandigarh.
- **Electrical Measurements**
- The dielectric measurement has been carried out using Agilent 4285A Precision LCR meter at H.P.University, Shimla.

- The dc resistivity measurement has been carried out by using Keithley 2611 system at H.P.U. Shimla.

- **Magnetic Measurements**
  - The initial permeability and relative loss factor measurements have been carried out by using Agilent 4285A Precision LCR meter at H.P.U. Shimla.
  - The magnetic hysteresis measurements have been performed using a commercial available Vibrating Sample Magnetometer (LakeShore, Model 7140, USA) at Instituto de Fisica Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP) Campinas, 13083-859, SP, Brazil.
  - The Mössbauer spectroscopy has been done in Department of Physics Himachal Pradesh University Shimla, using a constant acceleration driven Mossbauer spectrometer using ^{57}Co (Rh) source. The spectrometer is calibrated using a natural iron foil.

❖ Plan of work

- A brief description of the contents of this thesis, which is divided into the five following chapters:
- Chapter 1: "Introduction" includes historical development, nature, chemistry, and structure of ferrites. It also includes the effect of substituted ions on the ferrites and aim of the present work.
- Chapter 2: "Theoretical background" gives the relevant theoretical background and formulae required for the study of structural, electrical, dielectric, magnetic and Mössbauer properties of ferrites under investigation.

- Chapter 3: "Experimental details" deals with the methodology of sample preparation and describes the various experimental procedures and techniques employed for the study of the properties of these ferrite samples.
- Chapter 4: "Results and discussion" describes the measured structural, electrical, dielectric, magnetic and Mössbauer properties of the samples under study.
- Chapter 5: "Conclusion and suggestions" presents a basic summary of the results obtained from the present work. It will also have suggestions for future work in the field.

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List of Publication

1. ***Effect of In^{3+} ions doping on the structural and magnetic properties of $Mg_{0.2}Mn_{0.5}Ni_{0.3}In_xFe_{2-x}O_4$ spinel ferrites***

Satish Verma, Jagdish Chand, M. Singh, **Journal of Magnetism and Magnetic Materials** **324** (2012) 3252-3260.

2. ***Mixed Mg-Mn ferrites for high frequency applications processed by citrate precursor techniques***

Gagan Kumar, Jagdish Chand, ***Satish Verma*** *, M. Singh*, J. Phys. D. Appl. Phys. **42**(2009)155001.

3. ***Study of Structural and Magnetic Properties of In^{3+}Substituted Mg-Mn-Ni Spinel Ferrites***

Satish Verma*, M. Singh*

AIP Conf. Proc. 1349, 1137-1138(2011); doi: 10.1063/1.3606271 © 2011 American Institute of Physics 978-0-7354-0905-7/

4. ***Study of Structural, electrical and magnetic properties of Al^{3+} ions doped $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ spinel ferrites for high frequency applications***

Satish Verma*, Jagdish Chand, Pawan Kumar and M. Singh*

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5. ***Electrical and Magnetic Properties of nanosized $Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$ ferrites***

Satish Verma, Jagdish Chand, Pawan Kumar and M. Singh

AIP Conf. Proc. **1447** (2012)1099-1100.

6. ***Improvement in electric, dielectric and magnetic properties of $MgGd_{0.05}Fe_{1.95}O_4$ ferrites processed by solid state reaction technique***

*Jagdish Chand, **Satish Verma**, Pawan Kumar, Gagan Kumar and M. Singh*

AIP Conf. Proc. 1393, 107 (2011); doi: 10.1063/1.3653632 © *2011 American Institute of Physics 978-0-7354-0963-7/*

7. ***Room Temperature Ferromagnetic Ordering in Lanthanum Substituted Nano-Cobalt Ferrite***

*Pawan Kumar, Jagdish Chand, **Satish Verma**, M. Singh*

AIP Conf. Proc. 1393, 213 (2011); doi: 10.1063/1.3653632 © *2011 American Institute of Physics 978-0-7354-0963-7/*

8. ***Al^{3+} vk;uksa ls çfrLFkkfir eSxuhf'k;e-eSxuht-fudy QSjkbZV dh lajpukRed vkSj eSXusfVd xq.kksa dk v/;;u***

lrh'k oek]Z txnh'kpan] ioudqekj] vkSj egkohjflag, HkkSfrdfoHkkx]fgekpyçns'kfo'ofo|ky; National Scientific & Technical Seminar Proceeding: pp 41-43 (2012), Terminal Ballistic Research Laboratory, DRDO Chandigarh.

9. ***Structural, Electric and Dielectric Properties of MgFe2O4 Ferrite Processed by Solid State Reaction Technique***

*J. Chand, **Satish Verma**, P. Kumar and M. Singh*

International Journal of Theoretical and Applied Science **3**(2): 8-9(2011)

10. ***Micro-Structural Studies of Gadolinium Doped Cobalt Ferrites***

*P. Kumar, J. Chand, **Satish Verma**, M. Singh*

International Journal of Theoretical and Applied Science **3**(2): 10-12(2011).

11. ***Structural, magnetic and Mössbauer spectral studies of aluminum substituted Mg-Mn-Ni ferrites ($Mg_{0.2}Mn_{0.5}Ni_{0.3}Al_yFe_{2-y}O_4$)***

Satish Verma, Jagdish Chand and M. Singh

[Paper under review in the Journal of Alloys and Compound]

12. ***Electrical and magnetic characterization of nanocrystalline Al^{3+} ions doped Mg-Mn-Ni ferrite synthesis by citrate precursor route***

Satish Verma, Jagdish Chand and M. Singh

[Paper under review in the Journal of Alloys and Compound]

Presentation in Seminars, Conferences, Symposium, Workshops

1. 50th DAE-Solid State Physics Symposium, 5-9 December, 2005 at BARC Mumbai. **Low temperature processing and enhancement of electrical properties of mixed Mg-Mn ferrites.** B.S.Chauhan, Gagan Kumar, Satish Verma, Sangeeta Thakur, S.C. Katyal, M.Singh.

2. International Conference on *Magnetic Materials and their application for 21st Century* [MMA21], 21-23rd October, 2008 at National Physical Laboratory, New-Delhi[Paper Presented].

3. Contact Meeting for Popularizing the National Fusion Progamme [CMPNFP-08], 29th September, 2008 at NIT, Hamirpur (H.P), organized by Department of Applied Science and Humanities in association with Board for research in Fusion Science and Technology.

4. International Conference on *Multifunctional Oxide Materials* [ICMOM], 16-18th April, 2009 at Physics Department, H.P.University,Shimla [Paper Presented].

5. National Seminar on *Nuclear Technology for Sustainable Development* [NTSD09], 10-12th October, 2009 at Thapar University, Patiala.

6. 55th DAE-Solid State Physics Symposium, 26-30th December, 2010 at Manipal University, Manipal, Karnataka [Two papers published in American Institute of Physics].

7. Workshop on *Characterization Tools for Materials*, 22th February, 2011 at Punjab University, Chandigarh.

8. International Conference on Advances in Condensed and Nano Materials [ICACNM-2011], 23-26th February, 2011 at Punjab University, Chandigarh [Three papers published in American Institute of Physics].

9. Workshop-cum-Seminar on *Microscopic Techniques in Nano Science* [WSMTN-11], 30th March to 5th April,2011 at Physics Department, H.P.University,Shimla.

10. National Conference on *Recent trends in Materials Science* [RTMS-2011], 08-10th October, 2011 at Japee University of Information Technology, Wakanaghat, Solan-H.P [Paper Submitted].

11. 56th DAE-Solid State Physics Symposium, 19-23th December, 2011 at SRM University, Chennai, Tamilnadu [One paper published in American Institute of Physics].

12. National Conference on *Material Science and Technology: Current Trends and Future Prospects*, 6-7th February, 2012. Department of Physics and Chemistry, Lachoo Memorial College of Science and Technology, Jodhpur, Rajasthan [Paper Presented].

13. International Conference on *Frontiers in Nanoscience, Nanotechnology & their Applications,* [NanoSciTech-2012], 16-18 February, 2012 held at Punjab University, Chandigarh [Paper Presented].

14. N**ational Seminar on** *Experimental & Computational Techniques in Material Science* [ECTMS-2012], March 31st to 2nd April, 2012 held at Himachal Pradesh University, Shimla [Paper Presented].